Charge storage performances of micro-supercapacitor predominated by two-dimensional (2D) crystal structure

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Abstract

How to develop a high-energy-density supercapacitor still remains a big
challenge to us. Herein, we employ two new “anion intercalation materials” to
fabricate the asymmetric micro-supercapacitor with a high energy density. It is found
that both $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrodes show high
charge/discharge rates and excellent cycling stabilities (99.7% and 95.1% capacitance
retention after 10,000 cycles, respectively). Amazingly, the micro-supercapacitors
fabricated by $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ display the high
energy densities of 0.125 and 0.048 mWhcm⁻³ at a power density of 53 mWcm⁻³. In

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1 consideration of a lower BET area ($1 \text{ m}^2 \text{ g}^{-1}$) and a higher electric resistance (1.06Ω)
2 of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ than those ($2.2 \text{ m}^2 \text{ g}^{-1}$, 0.78Ω) of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$, the
3 higher energy density of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ is mainly attributed to the
4 unique two-dimensional (2D) extended $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ layer structure that favors for
5 charge insertion. This contribution demonstrates that it is the crystal structure of
6 material but not conventional BET area and electrical conductivity that decides the
7 electrochemical performances of micro-supercapacitors, which has been unknown
8 before. We can expect that unique two-dimensional (2D) extended layer material
9 could be a new candidate for next-generation supercapacitor.

10 **Keywords:** Two-dimensional (2D); Anion intercalation; Layered structure;
11 Asymmetric micro-supercapacitor

1. Introduction

Due to the deficiency of fossil energy and serious concern of environmental protection, the need for renewable energy sources has attracted great attention in recently years [1-3]. Up to now, electrochemical energy storage devices have been studied widely to meet the current great energy demands [4-7]. Specifically, supercapacitors, as the high-performance energy storage devices, have received considerable attention, since they can store more energies than conventional capacitors, and have much higher power density than batteries [8-11]. According to energy storage mechanism, supercapacitors are usually classified as electrical double layer capacitors (EDLC) and pseudo-capacitors. The former is based on electrostatic charge diffusion and accumulation at the electrode/electrolyte interface, which is mainly limited by the available surface area and electrical conductivity of materials. Nevertheless, the latter is mainly based on fast and reversible redox reactions, which suffers from the irreversibility of Faradic reactions and poor electrical conductivity of electrode materials [12-14]. Generally, the energy densities of supercapacitor are lower than battery [15-18]. Hence, it still remains a big challenge to develop a high-energy-density supercapacitor, so as to meet the practical demands. The energy density (E) of supercapacitor can be calculated according to Equation (1) as follows [7,19-22].

$$E = 0.5CV^2 \quad (1)$$

where C , V are the specific capacitance and the operating cell voltage of device, respectively. It is obvious that a high E value can be achieved by maximizing the C and V values; and also that the E value is affected more significantly by the operating cell voltage. Thus an efficient way to gain this goal is to develop a reasonable

1 asymmetric supercapacitor (ASC) by employing two different materials as the
2 positive and negative electrodes. Since these two electrodes materials have different
3 capacitance and electric potentials, ASC can fully utilize the high specific
4 capacitances and the wide potential windows. As a result, the maximum operating
5 voltage and specific capacitance can be achieved [23,24]. In this case, ASC would not
6 only have a high power density like conventional capacitors [23,25-27], but also have
7 a high energy density like batteries. It is desirable to develop new, suitable electrode
8 materials.

9 Up to now, the intercalation materials, usually used as the positive electrode in
10 lithium ion battery, have been extensively studied because of its high energy density
11 [28]. For anion intercalation materials, however, their relationship between structures
12 and electrochemical properties has not been established well. Typically, the
13 bismuth-containing anion intercalation materials, including BiOX (X=F, Cl, Br, I)
14 [29], $\text{Bi}_2\text{O}_2[\text{BO}_2(\text{OH})]$ [30], $\text{Bi}_2\text{O}_2\text{CO}_3$ [31], $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ [32],
15 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ [33], have not been investigated as the electrodes. In particular, for
16 $\text{Bi}_2\text{O}_2[\text{BO}_2(\text{OH})]$ [30] and $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ [32], $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ [33], the
17 featured $(\text{Bi}_2\text{O}_2)^{2+}$ /anion layered structure is believed to produce an internal electric
18 field [33]. Besides, they are also found to possess the hybridized band structures on
19 account of the lone pair electrons of Bi(III), which is greatly conducive to the charge
20 transport [33]. Furthermore, the hydroxyl-containing compounds have also been
21 reported to have an excellent pseudo-capacitive behavior [9].

22 In addition, anion group usually consist of nonmetal elements (*e.g.*, N, O, F, *etc.*),
23 these nonmetal elements carry the lone pair of electrons and can easily combine with
24 cations, which is beneficial to store more charges. Although some of anion
25 intercalated materials containing bismuth have been studied as the photocatalyst, they

1 have not been investigated as the electrochemical electrodes or devices up to now.
2 Herein, we, for the first time, have demonstrated that the bismuth-based anion
3 intercalation compounds can be used to fabricate the micro-supercapacitor with an
4 excellent volumetric energy density.

5 In this work, the $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ were
6 employed to fabricate micro-supercapacitors on base of their distinguishing
7 crystallographic feature, with a unique 2D electrical $[\text{Bi}_2\text{O}(\text{OH})_2^{2+}]_n$ layer. It was
8 found that the $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ have the low
9 charge-transfer resistances (1.06 and 0.78 Ω); and that they show a fast
10 charge/discharge rate and a high cycling stability (99.7% and 95.1% capacitance
11 retention after 10,000 cycles, respectively). To the best of our knowledge, this is the
12 first report on the supercapacitive properties of bismuth-based anion intercalation
13 compounds. The contribution demonstrates that it is the crystal structure of material
14 but not conventional BET area and electrical conductivity that decides the
15 electrochemical performances of supercapacitors, which has been unknown before.

2. Experimental

2.1. Sample preparation

$[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$. The pristine $[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$ was synthesized by a simple hydrothermal method. Typically, 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 40 ml distilled water, then the solution was stirred at room temperature for 10 min by magnetic stirrer. After the uniform solution transferred to a 50 ml Teflon-lined autoclave, the autoclave was heated at 180 °C for 24 h. After completion of the reaction, the sample was washed with distilled water for several times and dried at 60 °C for 5h.

$Bi_2O(OH)_2SO_4$. In a typical procedure, an aqueous solution was prepared by mixing with 15 ml distilled water and 15 ml 30 wt-% H_2O_2 . 1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in that aqueous at room temperature for 30 min by a magnetic stirrer. After 1 mmol of the Na_2SO_4 powder was added to the solution, then the mixture stirred for 30 min to form a uniform solution. After that, the mixture was transferred into a Teflon-lined stainless steel autoclave and maintained at 120 °C for 24 h. The as-obtained sample was then washed with distilled water for several times and dried at 60 °C for 5h.

2.2. Characterization

The morphologies of the samples were characterized by scanning electron microscope (SEM, Hitachi, SU-1510) using an accelerating voltage of 15 kV. The fine surface structures of the samples were characterized by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) equipped with an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. The

crystal phases of the samples were characterized by X-ray diffraction (XRD, Rigaku D/max-2550VB) with graphite monochromatized Cu K_α radiation (λ= 0.154nm). The surface areas of the samples were calculated by the Brunauer–Emmett–Teller (BET) method.

2.3. Electrochemical Measurements

All the electrochemical measurements were carried out on a CHI 660D electrochemical Working Station at room temperature. For a standard three-electrode cell, a 1 M KOH aqueous solution was used as the electrolyte. Carbon fibers was used as the current collector of working electrode (with an area of 0.25 cm²), Pt wire (diameter: 0.1 cm, length: 4 cm) and Hg/HgO (S.C.E) electrodes were used as the counter and reference electrodes. To fabricate the working electrode, 80 wt% of active materials ([Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O or Bi₂O(OH)₂SO₄), 10 wt% of acetylene black (conductivity agent) and 10 wt% of vinylidene fluoride (binder) were dispersed in 1-methyl-2-pyrrolidinone to form a homogeneous slurry. Then the slurry was dotted on the carbon fibers and dried for 24 h at room temperature. The mass of active material ([Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O or Bi₂O(OH)₂SO₄) on the carbon fibres is 2 mg. Cyclic voltammetry (CV) and chronopotentiometry (CP) were conducted in a potential range of 0-0.8 V and 0-0.6 V (vs. S.C.E), respectively. Electrochemical impedance spectroscopy (EIS) was performed from 0.1 Hz to 100 KHz at an open circuit potential and an alternating current (AC) voltage amplitude of 5 mV. Areal and specific capacitances were calculated using the following Equations (2) and (3), respectively,

$$C_a = I \cdot t / (\Delta V \cdot S) \quad (2)$$

$$C_{sp} = I \cdot t / (\Delta V \cdot m) \quad (3)$$

1 where I is the constant discharge current, t is the discharging time, ΔV is the voltage
2 drop upon discharging (excluding the IR drop), m is the mass of the active material,
3 and S is the geometrical area of the electrode.

4 To fabricate the asymmetric micro-supercapacitor, the flexible, conductive
5 carbon fibers were also used as the current collector [7,34]. The working electrodes
6 for micro-supercapacitors were fabricated by the similar procedures to those for
7 three-electrode test. It is noted that for micro-supercapacitors the mass of active
8 material ([Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O or Bi₂O(OH)₂SO₄) on the carbon fibers is 5
9 mg, which is different from that for three-electrode test. The negative electrode of
10 micro-supercapacitors is fabricated as follows: 2 mg of activated carbon was
11 dispersed in 1 mL ethanol under sonicating. After 30 min, a homogeneous ink formed;
12 then, 50 μ L of homogeneous ink was coated onto the carbon fibers, in which 0.1 mg
13 of activated carbon was contained.

14 To fabricate the asymmetric micro-supercapacitor, the active material
15 ([Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O or Bi₂O(OH)₂SO₄)/carbon fiber was employed as the
16 positive electrode, the activated carbon/carbon fiber was employed as the negative
17 electrode, and 1M KOH aqueous solution was used as the electrolyte. The fabrication
18 process of asymmetric micro-supercapacitors is shown in Fig. S1 (Seeing electronic
19 supporting information (ESI[†])). First, the activated material
20 ([Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O or Bi₂O(OH)₂SO₄) and activated carbon were coated on
21 the carbon fibers, respectively; then one piece of cellulose paper (as separator) was
22 used to package the activated carbon coated electrode (negative); finally, the

1 micro-supercapacitor was assembled by encircling the negative electrode with the
2 positive electrode. In order to prevent the leakage of electrolyte, one piece of plastic
3 film was used to package the micro-supercapacitor, then 1 M KOH aqueous solution
4 was injected. The volume of our asymmetric micro-supercapacitors is 0.023 cm³. The
5 mass ratio of positive and negative electrodes is based on the charge balance theory (q^+
6 $= q^-$), which depends on specific capacitance (C), potential range (ΔV), and the mass
7 of active materials on electrodes (m), namely, $q = mC\Delta V$. In order to ensure $q^+ = q^-$,
8 the mass balance follows the Equation of $\frac{m^-}{m^+} = \frac{C^+ \Delta V^+}{C^- \Delta V^-}$.

9 **2.4. Theory calculations**

10 All calculations were carried out using the density of functional theory (DFT)
11 with the exchange-correlation function described by GGA-PBE [35]. A (1×1) super
12 cell of [Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O or Bi₂O(OH)₂SO₄ was used and enabled by the
13 CASTEP package in Materials Studio, in which the projector augmented wave (PAW)
14 method represented the electron-ion interaction with a kinetic energy cutoff of 450 eV
15 after convergence calculation [36,37]. During optimizations, the energy and force
16 converged to 10⁻⁴ eV/atom and 10⁻³ eV/Å, respectively. The k -points were 5×3×5,
17 5×1×1 and 1×5×1 for the super cells of bulk super cells respectively. In energy and
18 DOS calculations, the k -points increase to 9×3×9, 9×3×1 and 3×9×1 for bulk super
19 cells, respectively. To generate 13 k -points by Line-mode, between the each
20 connecting specific points of the Brillouin zone for the band of energy calculations.
21 The vacuum in all the models was kept at 12 Å.

3. Results and discussion

3.1. Featured layered structure

Fig. 1(a,b) shows that $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ consists of NO_3^- anions groups and two-dimensional (2D) $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ polycation layer, which has a tetragonal space group *CMC21* with the unit cell parameters of $a = 5.3878 \text{ \AA}$, $b = 5.3984 \text{ \AA}$, $c = 17.136 \text{ \AA}$ and $\alpha = \beta = \gamma = 90(3)^\circ$ [32]. It has a featured layered structure, in which the anions layers alternatively intercalate between the polycation layers. The $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ layers are constructed by Bi, O and H. According to crystallography of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$, each hydroxyl (OH) group connects one Bi atom, and each O atom connects three Bi atoms (Fig. 1c). It is obvious that the $[\text{Bi}_2\text{O}_2]^{2+}$ polycation layer extends along a 2D space, also shown in Fig. 1d. Thus, we could understand that the electrons can well transfer along 2D space, indicating a good conductivity of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$.

Besides, $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ has a monoclinic space group *P21/c* with the unit cell parameters of $a = 7.692(3) \text{ \AA}$, $b = 13.87(1) \text{ \AA}$, $c = 5.688(2) \text{ \AA}$ and $\beta = 109.01(3)^\circ$ [38]. Fig. 1(e,f) also presents its layered structure, which consists of sulfate anion groups and $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ infinite double chains. The $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ polycations double chains are constructed by Bi(1)-OH(1)-Bi(2)-O four-member ring and Bi(1)-OH(2)-Bi(2)-O-Bi(1)-O six-member ring. According to its crystallography, each hydroxyl (OH) group connects two Bi atoms and each O atom connects three Bi atoms. The coordination spheres of both Bi(1) and Bi(2) atoms are completed by the additional O of SO_4^{2-} anion. In particular, there is at least four OH around each SO_4^{2-} groups, and the OH(1)-O(4) distance is calculated to be $2.77(1) \text{ \AA}$ (Fig. 1g), indicating that a hydrogen bond can form between them, which helps to stabilize the whole

1 structure. It is noteworthy that the $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}$ chains can only extend along [001]
2 direction, as known from the common $[\text{Bi}_2\text{O}_2]^{2+}$ net structure in Aurivillius phase
3 (*e.g.*, Bi_2MoO_6 [39], Bi_2WO_6 [40], Bi_2SiO_5 [41], *etc.*) and Sillen phase (*e.g.*, BiOX ,
4 $\text{X}=\text{Cl}$, Br and I) [29]. The interesting characteristic has been reported to result from
5 the involvement of negative hydroxyl groups [31]. Moreover, the $[\text{Bi}_2\text{O}_2]^{2+}$ chains and
6 anion parallel each other with an interlaced arrangement along [001] direction. It is
7 obvious that for $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$, the $[\text{Bi}_2\text{O}_2]^{2+}$ chains extend along a one-dimension
8 (1D) space, as also shown in Fig. 1h. We could understand that the electron transfer
9 easily occurs along 1D direction, indicating a good conductivity of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$.

10 In order to estimate the charge distribution for $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and
11 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$, we have resorted to density functional theory (DFT) using Material
12 Studio software. The total density of states (TDOS) and the partial DOS (PDOS) are
13 employed to explore the electronic properties of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and
14 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ Fig. S2 (Seeing ESI[†]). For both $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and
15 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$, the calculated electronic densities of states (DOS) are close to Fermi
16 level (E_F), signing a good electrical conductivity [8,42].

17 Moreover, their real-space electrons densities of oxygen show the pronounced
18 maxima among the Bi, O and N (or S), as shown in Fig. S3 (Seeing ESI[†]). Chemically,
19 the electron density presents a multi-centre bonding situation, so we can observed that
20 both NO_3^- and SO_4^{2-} anions show an obvious multi-centre bonding situation,
21 suggesting that the anions are easily to combine with the other cations, that is, the
22 anion group easily attract more charges. Aydinol *et al.* have reported that more
23 charges can be transferred according to the intercalation of lithium ions in electrode
24 materials [43]. Liu *et al.* have reported that a new charge compensation mechanism, in
25 which oxygen can provide an excellent pseudo-capacitance [10]. Li *et al.* have done

excellent work in flexible supercapacitors [7,17,18,34]. In fact, the role of anion used for charge compensation has not been well established [10,44,45]. Summarily, these layered structures are attractive for charge storage, because they can provide more ion intercalation sites [44,45].

In our experiments, we acquired the phase-pure $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ by a simple hydrothermal method. Fig. 2 shows the X-ray diffraction (XRD) of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ samples. All their diffraction peaks are well in agreement with the standard cards (JCPDS 53-1038: $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$, JCPDS 45-439: $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$). No impurities peaks of $\text{Bi}(\text{OH})_3$ or BiO_3 or Bi are observed, indicating the formation of phase-pure $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$. Their scanning electron microscopy (SEM) images (Fig. S4, Seeing ESI[†]) show the formation of large $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ particles and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ microrods, respectively. The high-resolution transmission electron microscopy (HRTEM) images of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ are presented in Fig. S5 (seeing ESI[†]). The lattice spacings of 0.3126 and 0.2922 nm correspond to the (103) and (006) facets of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$, respectively; and the lattice spacing of 0.2783 nm corresponds to the (-112) facet of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$, suggesting that the microrod growth preferentially along [-112] direction. The selected-area electron diffraction (SAED) patterns further reveals the polycrystalline nature of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and single-crystalline nature of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$. Finally, $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ have low BET area (1 and 2.2 m² g⁻¹).

3.2. Electrochemistry properties of electrodes

Furthermore, we have employed $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ as the active materials to fabricate electrodes. Their electrochemical properties are investigated mainly by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) in a conventional three-electrode system. Herein, the $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ (or $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$) coated on carbon fibers, Pt wire and standard saturated calomel electrode (S.C.E.) were used as the working electrodes, counter electrode and reference electrode, respectively; and 1M KOH aqueous solution was used as the electrolyte. All the electrochemical measurements were performed on a potentiostat/galvanostat station (CHI 660D). The CV measurements were performed between 0 and 0.8 V (vs. SCE) at different scanning rates (Fig. 3(a,c) and Fig. S6 (a,c)((seeing ESI[†]))). It shows that our electrode has a good electrochemical stability. Their featured CV curves indicate the ideal capacitive behaviors and fast charge/discharge rates [9].

The galvanostatic charge-discharge measurements were also performed between 0 and 0.6 V (vs. SCE) at different current densities (Fig. 3(b,d) and Fig. S6 (b,d)((seeing ESI[†]))). The two curves show that there is nearly no internal resistance (IR) drop at the different current densities, confirming a good electrical conductivity. The symmetric charge-discharge curves suggest that the capacitance of electrode originates from the ion adsorption and accumulation at the interface of electrolyte/electrode.

The discharge capacitance can be calculated from the galvanostatic discharge curves using Equation (4) as follows:

$$C=It/SV=Jt/V \quad (4)$$

1 where C is the discharge capacitance (mFcm^{-2}), I is the discharge current (mA), t is
 2 the discharge time (s), S is the actual area (cm^2) of working electrode, V is the
 3 discharge potential (V), and J is the current density (mAcm^{-2}). As shown in Fig.
 4 3(b,d), the specific area capacitances of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ electrode are
 5 22.70, 21.66, 21.35, 21, 20.00 and 20.00 mFcm^{-2} at current densities of 0.1, 0.2, 0.5, 1,
 6 2, and 5 mAcm^{-2} , respectively. Under the same current densities, the specific area
 7 capacitances of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrode are 16.53, 14.83, 14.41, 13.83, 13.53 and
 8 12.3 mFcm^{-2} , respectively. The capacitive performances of our electrodes can be
 9 comparable to the results in the existing references [9,43-45], For example, 3.24
 10 $\text{mFcm}^{-2}/\text{H-TiO}_2$ (0.5 M Na_2SO_4) [9], 2.0 $\text{mFcm}^{-2}/\text{ZnO}$ nanowires (1 M Na_2SO_4) [46],
 11 1.38 $\text{mFcm}^{-2}/\text{H-ZnO}$ electrode (0.05 mAcm^{-2}) [47]. Furthermore, the Fig. S7 and Fig.
 12 S8 (use different current collector, seeing ESI[†]) shows the specific capacitances of
 13 $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrodes at different current
 14 densities. At the same current density of 0.1 mA cm^{-2} , $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$
 15 and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrodes are 2838 and 2066 mFg^{-1} , respectively. When the
 16 current density is increased to 5 mA cm^{-2} , $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ electrode can
 17 maintain ~88% of the initial capacitance (2838 mFg^{-1}), whereas $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$
 18 electrode can maintain ~75% (2066 mFg^{-1}). It shows the former electrode has a better
 19 rate capability than the latter.

20 We have also examined the cycling stability of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and
 21 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrodes. The electrodes were both tested at a scanning rate of 100
 22 mVs^{-1} for 10000 cycles. Fig. S9 and Fig. S10 (use different current collector, seeing
 23 ESI[†]) presents the 1st, 5,000 th and 10,000 th cycle curves of two electrodes. It is
 24 obvious that the first and 10000 th the CV curves are almost same. As shown in Fig.
 25 4b and Fig. S11 (use different current collector, seeing ESI[†]), after 10,000 cycles, the

discharge capacitances of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrodes only decreased by 0.3% and 4.9%, respectively. The results demonstrate a good cycling stability of our electrodes.

3.3. Electrochemistry performances of asymmetric micro-supercapacitors

To evaluate actual application performances of electrodes, the asymmetric micro-supercapacitors were fabricated by using $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ /carbon fiber (or $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ /carbon fiber) and activated carbon/carbon fiber as the cathode and anode, respectively. Herein, 1 M KOH solution was used as the electrolyte and one piece of cellulose paper as the separator, and the average volume of our asymmetric micro-supercapacitor is about 0.023 cm^3 . Fig. 5a illustrates the geometric configuration of the asymmetric micro-supercapacitor. Fig. 5b shows the CV curves at a scanning rate of 10 mVs^{-1} for the two optimized micro-supercapacitors fabricated by $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$. Moreover, their CV curves at different scanning rates are presented in Fig. 6(a,c). The cell voltage (1.0 V) of our micro-supercapacitor is as high as conventional active carbon (AC)-based symmetric capacitors in aqueous electrolytes (0.8-1.0 V). Fig. 5c gives the typical galvanostatic charge/discharge curves of two micro-supercapacitors at a current density of 6.7 mA/cm^3 , and Fig. 6(b,d) presents their galvanostatic charge/discharge curves at different current densities. We have assembled two micro-supercapacitors in series and examined their power capabilities. It is found that after being charged for 5 s, our device can efficiently power a 5 mm-diameter red round light-emitting diode (LED) for more than 30 s (Fig. 5d). Fig. 5e further presents the Ragone plots of two micro-supercapacitors. The energy density (E) and power density (P) of device can be calculated using Equations (6) and (7) as follows:

$$E = \int (I \Delta v(t) dt) / (V) \quad (6)$$

$$P = E / \Delta t \quad (7)$$

where I is the discharging current, $\Delta v(t)$ is discharging voltage excluding the IR drop, dt is time differential, V is the volume of entire micro-supercapacitor, and Δt is the discharging time. When the power density increases from 6.7 to 53 mW/cm³, the energy density of [Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O-based micro-supercapacitor decreases from 0.125 to 0.064 mWh/cm³; whereas the Bi₂O₂(OH)₂SO₄-based one decreases from 0.048 to 0.015 mWh/cm³. Comparison of this work with previously reported results on those based-volume supercapacitors (Table S1, seeing ESI[†]), it is obvious that the energy densities of our micro-supercapacitors are higher than those of graphene-based supercapacitor (0.06 mWh/cm³, PVA/H₃PO₄) [48], TiN supercapacitor (0.05 mWh/cm³, PVA/KOH) [49], single walled carbon nanotube supercapacitor (0.01 mWh/cm³, PVA/H₃PO₄) [50] and multiple-walled carbon nanotube super capacitor (0.008 mWh/cm³, PVA/ H₂SO₄) [51]; but obviously lower than those of Co₉S₈//Co₃O₄@RuO₂ array asymmetric super capacitor (1.21 mWh/cm³, PVA/KOH) [20] and NiCo₂O₄ nanosheets coaxial-type fiber super capacitor (1.44 mWh/cm³, PVA/KOH) [52]. It should be noted that the expensive materials or complicate preparation or toxic materials are used for the latter two supercapacitors. Finally, we have investigated the cycling stabilities of our asymmetric micro-supercapacitors for 10,000 cycles, which has been rarely demonstrated for aqueous electrolyte-based asymmetric micro-supercapacitors. Fig. 5f shows that after 10,000 cycles, the 76.9% and 70.0% of specific capacitances are retained for [Bi₆O₆(OH)₃](NO₃)₃•1.5H₂O- and Bi₂O(OH)₂SO₄-based micro-supercapacitors. Their CV curves also confirm the high cycling stabilities (Fig. S12, seeing ESI[†]).

Further, we have investigated the electrochemical impedance spectroscopy (EIS) of our micro-supercapacitor. Fig. 7 and Fig S13 (use different current collector, seeing ESI[†]) shows their Nyquist plots. The simulated equivalent electric circuit from EIS data consists of a solution resistance (R_s), a constant phase element (CPE) accounting for electrical double-layer capacitance, a charge-transfer resistance (R_{ct} , also called Faraday resistance), and a Warburg impedance (W) for the diffusion and insertion of K^+ ion into active materials. For our two supercapacitors, their resistances (R_s) of electrolyte solution are measured to be 5.25 Ω , suggesting that R_s is not susceptible to the surface condition of electrode. However, the R_{ct} values of $[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$ and $Bi_2O(OH)_2SO_4$ are calculated to be 1.06 and 0.78 Ω , respectively. This clearly demonstrates the reduced charge-transfer resistances (R_{ct}) for the anion intercalation materials. Moreover, the charge-transfer resistance (R_{ct}), is a limiting factor for supercapacitor [12,53]. Thus a low Faraday resistance of electrode material leads to a high areal power.

Herein, we have proposed a charge storage mechanism about two $[Bi_2O(OH)_2]^{2+}_n$ layered materials (Fig. 8). Comparing $[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$ with $Bi_2O(OH)_2SO_4$ (Fig. 1g,h), it is obvious that the $[Bi_2O_2]^{2+}$ polycation layer extends along a 2D space for $[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$, whereas the $[Bi_2O_2]^{2+}$ chains extend along a one-dimension (1D) space for $Bi_2O(OH)_2SO_4$. Moreover, the anion layers are paralleled with the $[Bi_2O_2]^{2+}$ polycation layers or the $[Bi_2O_2]^{2+}$ chains. Thus, we could understand that for $[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$, the electrons can transfer along the 2D plane, whereas along 1D direction for $Bi_2O(OH)_2SO_4$. In other words, the $Bi_2O(OH)_2SO_4$ has a higher conductivity than the former, since only the electron transfer along specified direction is effective. This is in agreement with our EIS results. For $[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$, however, its 2D $[Bi_2O_2]^{2+}$

1 polycation layer can offer more sites for ion intercalation, compared with the 1D
2 $[\text{Bi}_2\text{O}_2]^{2+}$ polycation chains of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$, namely, the 2D layer space of
3 $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ can accommodate more K^+ . Hence, the specific
4 capacitance of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ is much higher than that of
5 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$. The mechanisms are illustrated in Fig. 8. When the electrons transfer
6 along the 2D $[\text{Bi}_2\text{O}_2]^{2+}$ polycation layer space or the $[\text{Bi}_2\text{O}_2]^{2+}$ chains space, the K^+ in
7 electrolyte solution can be absorbed over the electrode interface and inserted into the
8 appropriate sites while charging; and vice versa while discharging.

9 Summarily, two new anion intercalation materials have high specific
10 capacitances (22.7 mFcm⁻² for $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and 16.53 mFcm⁻² for
11 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ at 0.1 mAcm⁻²). Remarkably, these anion intercalation materials show
12 a cycling stabilities (99.7% for $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and 95.1% for
13 $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ capacitance retentions after 10,000 cycles). Amazingly, the
14 $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ - and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ -based micro-supercapacitors show
15 high energy densities of 0.125 and 0.048 mWhcm⁻³ at a power density 6.7 mWcm⁻³,
16 respectively.

17 **4. Conclusions**

18 It has been demonstrated that the high energy density of
19 $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ is mainly resultant from the two-dimensional (2D)
20 extended $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ layer structure, which could offer more accommodating sites
21 for ion intercalation, instead of BET area and electrical conductivity. We can expect
22 that unique two-dimensional (2D) layered material could be a new candidate for
23 next-generation supercapacitor.

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Legends of Fig.s

Fig. 1. Crystal structures of (a-d) $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and (e-h) $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$: (a,d) Layer structure; (b) $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ polycations along a axis; (c) OH(1)-O(3) hydrogen bond; (e,h) Layer structure; (f) $[\text{Bi}_2\text{O}(\text{OH})_2]^{2+}_n$ polycations along a axis; (g) of OH(1)-O(4) hydrogen bond.

Fig. 2. XRD patterns of (a) $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and (b) $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$

Fig. 3. a) CV curves of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ electrode at various scanning rates; b) Galvanostatic charge-discharge curves of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ electrode at different current densities; c) CV curves of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrode at various scanning rates; d) Galvanostatic charge-discharge curves of $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrode at different current densities; notes: carbon fibers as current collector.

Fig. 4. Cycling performances of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrodes; notes: carbon fibers as current collector.

Fig. 5. Asymmetric micro-supercapacitors fabricated by $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ or $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ as positive electrode: (a) A structure photograph of and Schematic illustration of micro-supercapacitor; (b) CV curves of micro-supercapacitors at a scanning rate of 10 mVs^{-1} ; (c) Galvanostatic charge-discharge curves of micro-supercapacitor at a current density of 6.7 mAcm^{-3} ; (d) A photograph of two micro-supercapacitors in series lighting up LED indicator; (e) Volumetric energy density vs. power density for both micro-supercapacitors; (f) Cycling stabilities of both micro-supercapacitors running for 10,000 cycles.

Fig. 6. Electrochemistry performances of micro-supercapacitor fabricated by (a,b) $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and (c,d) $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ as positive electrode: (a,c) CV

1 curves at different scanning rates; (b,d) Galvanostatic charge-discharge curves at
2 different current densities.

3 **Fig. 7.** Nyquit plots (the inset of equivalent circuit) of $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$
4 and $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ electrodes in the frequency range from 0.1 Hz to 1000 kHz in 1M
5 KOH aqueous solution; notes: carbon fibers as current collector.

6 **Fig. 8.** Plausible charge storage mechanisms of (a) $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and
7 (b) $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

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Graphic Abstract

A high-energy-density micro-supercapacitor is developed by $[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ with unique 2D extended layer structure.